

2003 Blind Audit of EPA Protocol Gases

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Why are we giving this talk to a QA Audience ?

- ◆ EPA Protocol Gases are widely used gaseous reference standards
- ◆ QA professionals need to understand the uncertainty of these reference standards
- ◆ This program is a example of how EPA can assess a commercial product with minimal interference and reasonable cost
- ◆ Useful lessons about organizing an audit program and about gas metrology

Characteristics of EPA Protocol Gases

- ◆ They must be traceable to NIST reference standards (Standard Reference Materials)
- ◆ Anyone may use the protocol to certify compressed gas mixtures(vendors, users, gov't)
- ◆ A general, flexible analytical procedure
- ◆ A specific statistical analysis procedure
- ◆ Specific documentation requirements
- ◆ EPA conducts audits to determine their accuracy

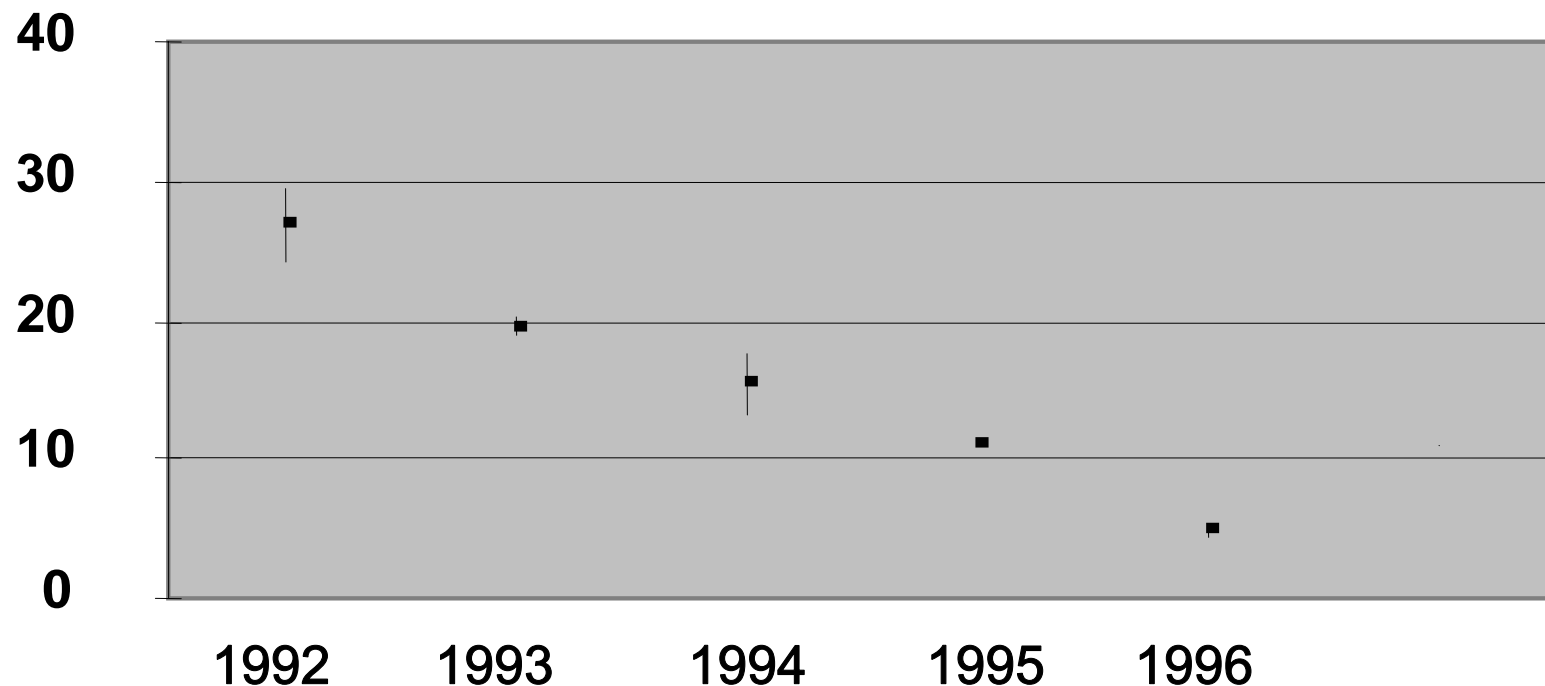
Why is there a need for the EPA Protocol Gas Audit Program ?

- ◆ EPA does not certify or permit specific organizations to produce these standards. Anyone can do so.
- ◆ EPA does not inspect or audit vendor facilities
- ◆ The protocol is a general analytical procedure. The analyst chooses specific procedures and then calculates the uncertainty of the measurements.
- ◆ The protocol does not have an acceptance criterion for the uncertainty of standards. The user specifies it. The Acid Rain Program specifies +/- 2 % accuracy.
- ◆ The audits are the only tool available for EPA to obtain an independent assessment of the uncertainty.

History of EPA Audit Program

- ◆ From 1985 to 1997, there were 253 audits
- ◆ 78% of standards accurate to within +/- 2%
95% of standards accurate to within +/- 5%
99% of standards accurate to within +/- 10%
- ◆ In 1995, one cylinder biased by -16.3%
- ◆ Strong utility and vendor support for audits
- ◆ Audit Program ended in 1998

Audits are strongly correlated with improved quality



Percentage not meeting acceptance criterion

2003 Audit of EPA Protocol Gases

- ◆ First audit in 7 years
- ◆ Blind audit (vendors didn't know)
- ◆ 14 national specialty gas vendors
- ◆ 42 tri-blend cylinders (3 per vendor)
- ◆ Similar audit procedures as in past
- ◆ SRMs and NTRMs used as reference stds.
- ◆ Mactec (primary audit lab) and Spectral Insights (reference audit lab)

Tri-blend EPA Protocol Gases

	CO ₂ (%)	NO (ppm)	SO ₂ (ppm)
Low	5	50	50
Medium	12	400	500
High	18	900	1000

Analytical Instrumentation

- ◆ NO - API Model 200AH chemiluminescence
- ◆ NO - Ametek Model 922M UV absorption
- ◆ SO₂ - Bovar Model 721M UV absorption
- ◆ CO₂ - California Analytical Model 3300A NDIR
- ◆ NO, SO₂, and CO₂ - Nicolet Model 760 FTIR
- ◆ Environics Series 3740 gas dilution system

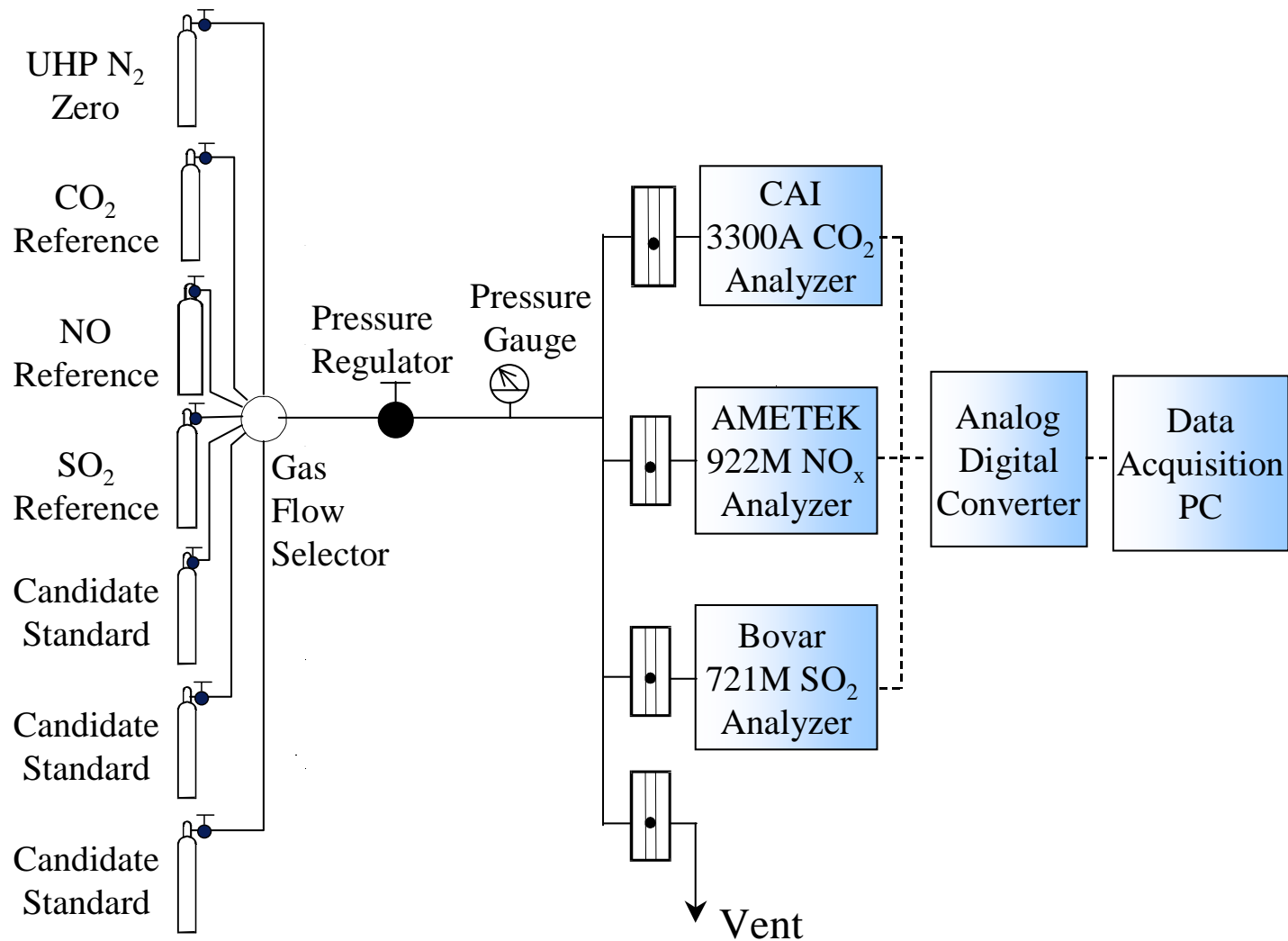
Mactec Lab



Instrumentation



Schematic of Mactec Apparatus



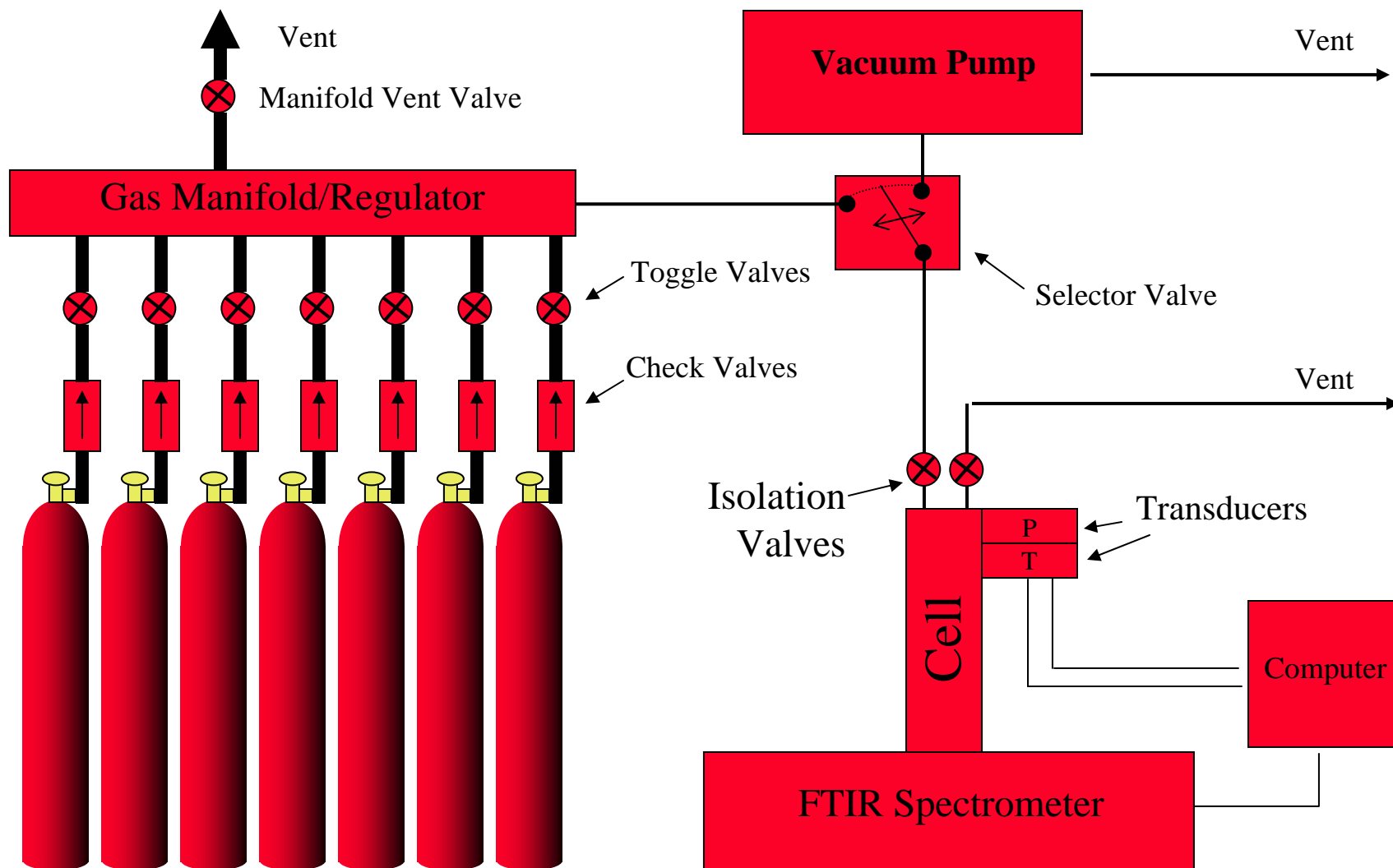
Spectral Insights Mobile FTIR Lab



Nicolet Nexus Model 760 FTIR



Spectral Insights Apparatus



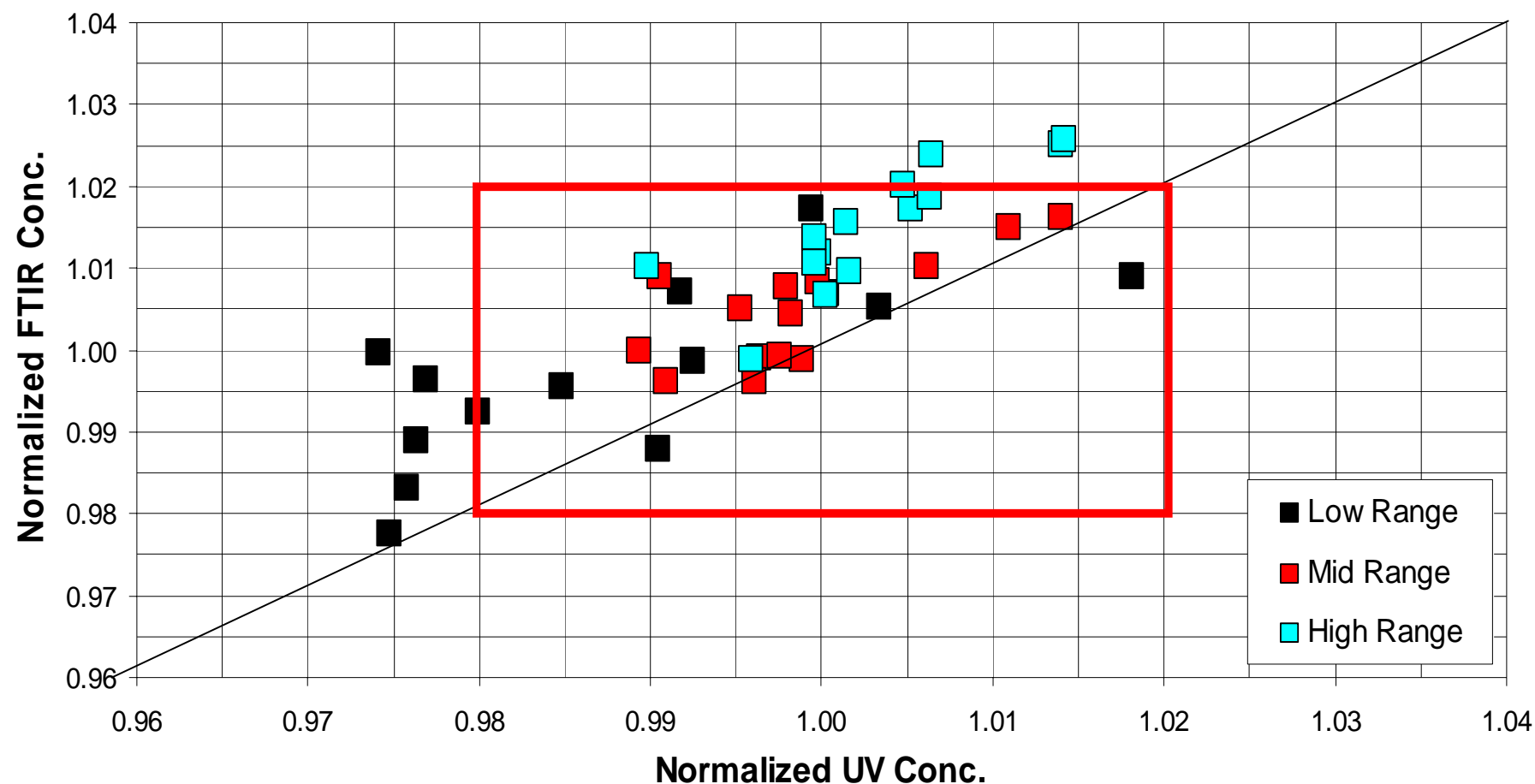
Instrumentation Problems

- ◆ High-level CO₂ SRM empty for FTIR analyses
 - FTIR lab prepared a high-level CO₂ primary ref. std.
 - EPA threw out the high-level CO₂ FTIR data
- ◆ NO data from chemiluminescent analyzer biased low due to CO₂ quenching
 - Chemiluminescent NO data thrown out
 - Measurements repeated with a NO UV analyzer

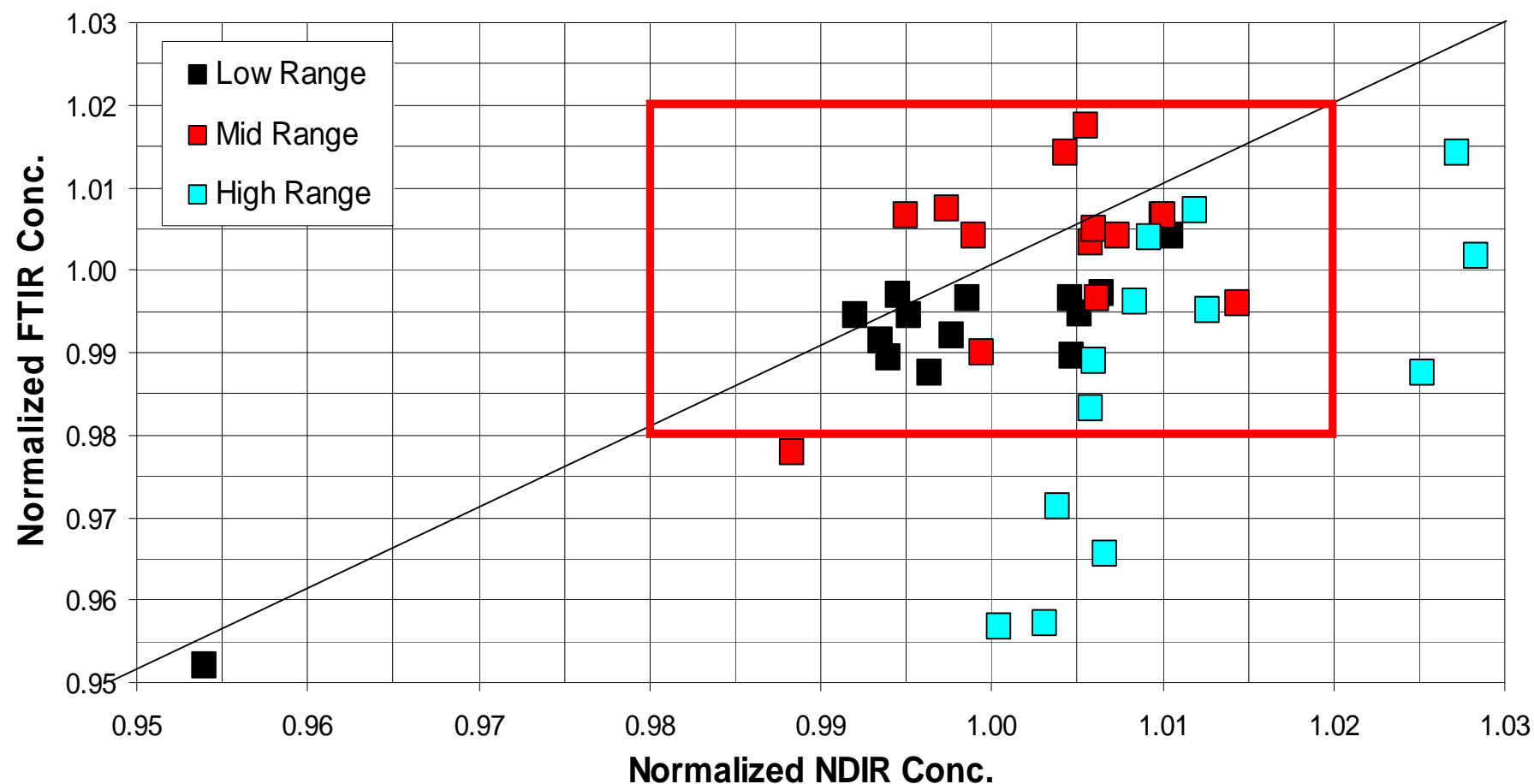
Instrumentation Problems

- ◆ NO UV analyzer set up for 0 - 500 ppm range, but should have been for 0-1000 ppm range
- ◆ SO₂ interfered with NO UV analyzer readings
 - Injected SO₂ in N₂ mixture to develop a interference correction equation for NO data, but curve for SO₂ and NO in N₂ mixture is very nonlinear at mid- and high-level concentrations
 - EPA threw out mid- and high-level NO UV data

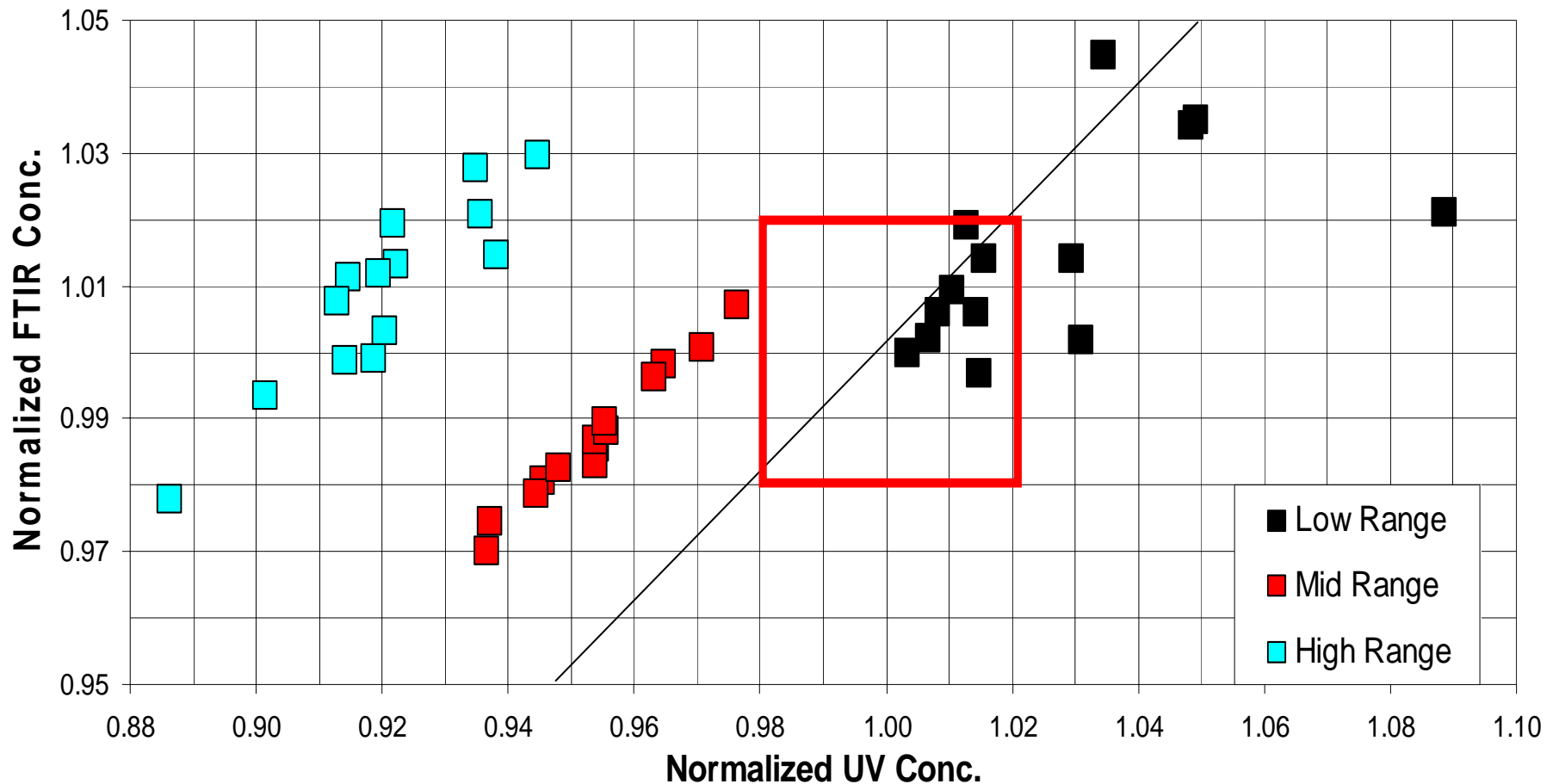
Comparison of FTIR Data with UV Data for SO₂ EPA Protocol Gases



Comparison of FTIR Data with NDIR Data for CO₂ EPA Protocol Gases



Comparison of FTIR Data with UV Data for NO EPA Protocol Gases



EPA Protocol Gases not meeting Acid Rain Program's Acceptance Criterion for One or Both Audit Analyses

	NO Analyses			SO ₂ Analyses			CO ₂ Analyses		
	UV	FTIR	Both	UV	FTIR	Both	NDIR	FTIR	Both
Low	6/14	4/14	4/14	6/14	1/14	1/14	1/14	1/14	1/14
Mid	- - -	3/14	- - -	0/14	0/14	0/14	0/14	1/4	0/14
High	- - -	3/14	- - -	0/14	3/14	0/14	3/14	- - -	- - -

Summary of Results

- ◆ Overall failure rate: 32 of 210 analyses (15%)
- ◆ SO₂ failure rate: 10 of 84 analyses (12%), worst bias 2.7%
- ◆ NO failure rate: 16 of 56 analyses (29%), worst bias -8.4%
- ◆ CO₂ failure rate: 6 of 70 analyses (9%), worst bias 5%
- ◆ All documentation requirements were met

Lessons Learned for Future Audits of EPA Protocol Gases

- ◆ Detailed audit SOPs are needed
- ◆ Audit labs need experience in gas metrology
- ◆ Instrumentation must be modified for gas metrology
- ◆ Traceability protocol needs to be modified for FTIR
- ◆ Gain experience with single component mixtures before moving to multicomponent mixtures
- ◆ Check multicomponent interference effects beforehand
- ◆ Intercompare audit labs before the audit starts
- ◆ Use an SRM or NTRM for FTIR measurements

Protocol Gas Audit Program Direction

- ◆ Scope
- ◆ Structure
- ◆ Funding
- ◆ Oversight
- ◆ Protocol Revision and Updates

Next Steps

- ◆ Detailed Outline
- ◆ Get feedback